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A Critical Assessment of Methods of Measuring the Rate of Corrosion of Steel in Reinforced Concrete

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Abstract:	In 1985, the Ontario Ministry of Transportation and Communications engaged Dr. Carolyn M. Hansson, of the Danish Corrosion Centre, as a researcher to: i) critically assess currently available electrochemical methods of determining the rate of corrosion of steel reinforcement in concrete, ii) identify promising techniques for Ministry use, in the laboratory and in the field, and iii) recommend an appropriate test procedure for the technique(s). This report summarizes Dr. Hansson's work, and includes her comments on her visits to research institutes and agencies carrying out corrosion rate measurements in Canada, the United States, Britain and Spain. Measurement techniques discussed include polarization resistance, E-Log I, AC impedance and electrochemical noise. Laboratory experiments carried out by Dr. Hansson are also described. The report concludes with recommendations for future testing.
Key words:	corrosion, reinforced concrete, corrosion rate, polarization resistance, AC impedance, E-log I, electrochemical noise treatment
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A Critical Assessment of Methods of Measuring the Rate of Corrosion of Steel in Reinforced Concrete

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NOTE TO THE READER

The ability to measure the rate of corrosion of reinforced concrete structures in the field would have a major impact on bridge management practices. The information would be useful in determining the priority of structures for repair, in selecting the repair method and monitoring its effectiveness and in establishing criteria for cathodic protection.

Several electrochemical test methods are used to measure the rate of corrosion of metals under laboratory conditions, but most are applicable to metals in solution. Researchers are now adapting these techniques to determine the corrosion of steel embedded in concrete. The actual test procedures differ from one researcher to another and, in some cases, the validity of the technique on reinforced concrete is uncertain.

This study was initiated to assess, through literature study and personal contact, the relative merits of techniques presently available and to recommend to the Ministry, the basis of a procedure which could be developed further for field use. A contract was awarded to the Danish Corrosion Centre in 1985, with Dr. Carolyn M. Hansson as the Principal Investigator. This report is a copy of Dr. Hansson's Final Report on the project to the Ministry.

It is intended that the format used will stimulate discussion and the Ministry will be pleased to receive comments from interested readers.

D.G. Manning,
Head, Materials Research.

A CRITICAL ASSESSMENT OF METHODS OF MEASURING THE RATE OF CORROSION OF STEEL IN REINFORCED CONCRETE

Final Report

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I. INTRODUCTION

The objectives of the project have been to critically assess the currently available electrochemical methods of determining the rate of corrosion of steel reinforcement in chloride contaminated concrete structures. A limited experimental program has been carried out and the different electrochemical techniques used and their advantages and disadvantages are described in Section II. In addition, visits have been made to five institutes actively involved with experimental measurement of corrosion of steel in concrete and a summary of these visits is given below in Section III in the order in which I made them. It should be noted that the conclusions given in this section are those of the personnel visited. My own conclusions and recommendations are given in Section IV.

II. ELECTROCHEMICAL TECHNIQUES FOR DETERMINING THE CORROSION RATE OF STEEL IN CONCRETE

Corrosion is an electrochemical process, ie. it involves transfer of charge from one species to another. For an electrochemical reaction to occur there must be two half cell reactions, one capable of producing electrons (the anodic reaction) and one capable of consuming electrons (the cathodic reaction). For steel in concrete, the anodic reaction is the dissolution or oxidation of iron and the cathodic reaction is usually the reduction of dissolved oxygen in the cement paste pore solution. During natural corrosion, the rates of these two reactions is equal and there is no net current arising from the electron exchange. Therefore, it is not possible to measure the corrosion current directly. In order to determine its value, the system must be shifted away from equilibrium so that the anodic and

cathodic reaction rates are not equal and a net current can be measured. This may be accomplished by applying a potential to the steel embedded in concrete and measuring the resulting net current flowing between the steel and a counter electrode which may also be embedded or may be external to the concrete. Alternatively, a current may be impressed between the steel and counter electrode and the resulting polarization of the steel measured. This procedure is fundamental to all electrochemical measuring techniqes but the method and ease of obtaining the actual corrosion rates and the accuracy of the results depends on technique used, as discussed below.

POLARIZATION CURVES

In this technique, the potential applied to the embedded steel is normally increased in the positive (anodic) direction either dynamically (potentiodynamically) or step-wise (potentiostatically) to a level of several hundred millivolts and the corresponding current monitored dynamically or at each step. The process is then repeated for negative values of the applied potential. When plotted in the form of potential (E) versus logarithm of the current (log i), the curve for passive steel has the form shown in Fig. 1a, whereas the curve for steel which is actively corroding due to the presence of chloride ions has the form shown in Fig. 1b[1]. Theoretically, the curves should exhibit a linear region at polarizations (ie. applied shifts in the potential from the corrosion potential) of 100 to 200 mV, the slopes of which are known as the Tafel slopes, $_a$ and $_c$, for the anodic and cathodic curves respectively. Extrapolation of these two regions to their common value at the corrosion potential, ie. zero polarization, gives the value of corrosion current, i_{corr}. This current can be directly converted to the corrosion rate if the area of corroding steel is known: 1 $A/m^2 \equiv$ 1.16 mm/yr. For steel in concrete, the linear regions do not normally exist and an exact value of the corrosion current is not possible. However, for laboratory specimens, it is relatively easy to obtain a corrosion current within one order of magnitude which, in the author's opinion, is all that one can expect in view of uncertainties in the area of embedded steel actually corroding.

Advantages of the polarization curve technique

The major advantage of polarization curve determination is that it is the only technique which gives any information about the steel's behaviour at potentials other than the immediate corrosion potential,

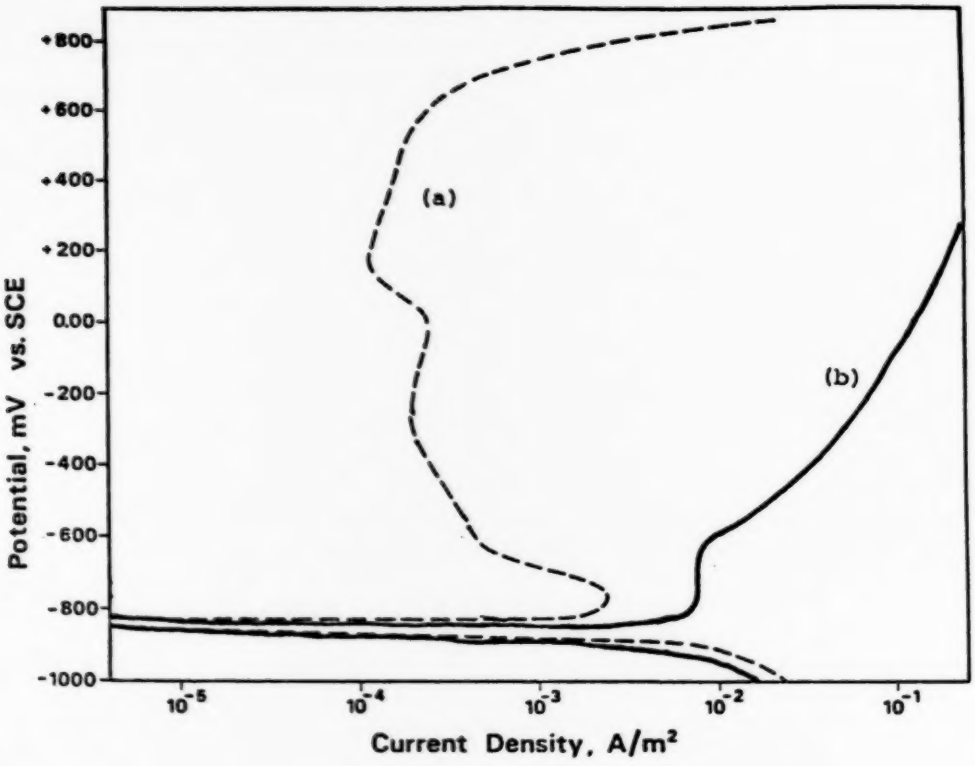


Fig. 1. Polarization curves for samples of steel in OPC mortar (a) immersed in $Ca(OH)_2$ solution and (b) immersed in a NaCl solution.

This is illustrated in Fig. 1 where the corrosion potential, E_{corr}, is similar for the two samples, -850 mV SCE, which is in a potential region where rapid active corrosion is not possible because of lack of dissolved oxygen[1,2]. Consequently, i_{corr} for the two samples is not significantly different. However, the curves illustrate the difference that would occur if, due to an increased access of oxygen, E_{corr} were to rise to a value of, for example, 0.0 mV SCE: the sample containing chloride would corrode nearly three orders of magnitude faster than the sample without chloride. The technique is well suited, therefore, to investigations of the effects of additives to the concrete[3,4], or changes in environment [5] on the corrosion behaviour of embedded steel or types of cement, etc. [6,7].

Disadvantages of the polarization curve technique

The major disadvantages of the technique are (i) that it takes a long time (hours or days) to perform and (ii) that it is necessary to

polarize the steel well away from its natural corrosion potential. It has been suggested [8,9] that such a large degree of polarization will change the environment at the steel/concrete interface to such a degree that the measurements will not accurately reflect the behaviour of the steel in its natural surroundings and that the test cannot be regarded as "non-destructive". In our experience, this is not so: while the test will inevitably change the value of E_{corr}, temporarily, it does not change the value of i_{corr} to any significant degree and E_{corr} drifts back to its original value after a period of time.

To illustrate this effect, the reproducibility of the measurements has been determined using 40 x 40 x 160 mm^3 mortar specimens containing an 8 mm ø steel rod. Polarization curves were obtained for three sets of 12 samples immersed in $Ca(OH)_2$ solution. The samples in Set A were polarized in 20 mV steps every two hours from their corrosion potential to +100 mV SCE (ie. to below the oxygen evolution potential), reversing the step direction to -800 mV SCE (ie., above the hydrogen evolution potential). In Set B, the scan was between +400 mV SCE (ie. above the oxygen evolution potential) and -800 mV. In Set C, the scan was between +100 mV and -1100 mV (ie. below the hydrogen evolution potential). Polarization curves were obtained for three samples in each set then, after 3 weeks, curves were obtained on the same three samples plus three additional samples. After a further two months, curves were obtained from nine samples in each set and, after another 3 months, on all 12 samples. The curves were measured again immediately in order to ascertain if there were any short term effects.

All the data from the first nine samples in Set C are shown in Fig. 2 to illustrate the level of scatter observed. The degree of scatter was similar for Sets A and B. As mentioned above, there was considerable scatter in the values of E_{corr} and this scatter was not systematic in terms of the number of times the samples had been polarized. The scatter in current at any particular potential was within an order of magnitude, however, which is as good as can be expected in as inhomogeneous a system as steel in concrete. Moreover, extrapolation of the curves to the free potential gives nearly the same value of i_{corr} for all the samples.

All the curves from one of the first three samples from each Set are given in Figs. 3 - 5 to show the effect of repeated measurements.

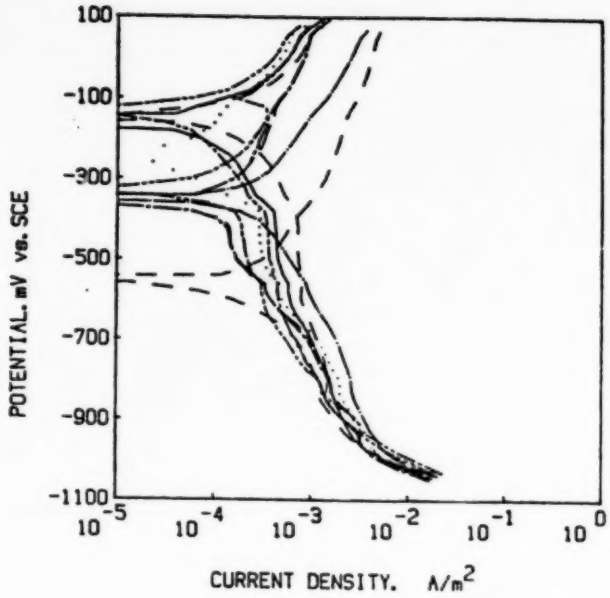


Fig. 2. Potentiostatic polarization curves for the first nine samples in Set C. Three of the samples had been tested once, three had been tested twice and three had ben tested three times.

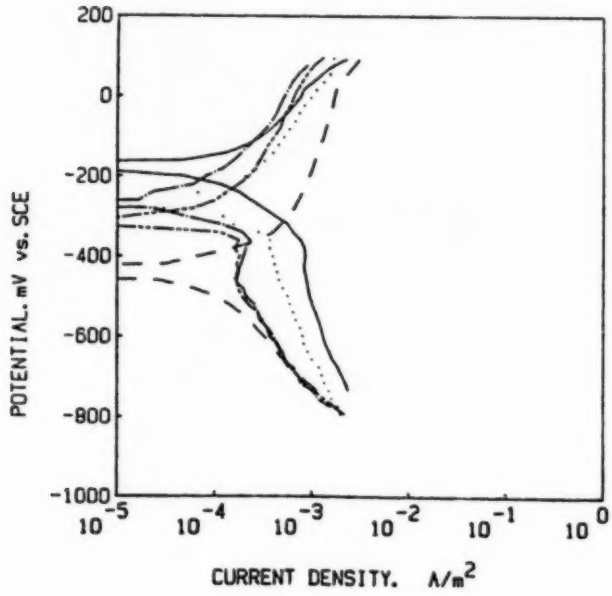


Fig. 3.Repeated polarization curves for one sample from Set A. The age of the sample at the beginning of the test was: curve 1————12 weeks; curve 2 ..... 15 weeks, curve 3-------- 22 weeks; curve 4 —·—·—·— 33 weeks; curve 5—·—·—·— 35 weeks.

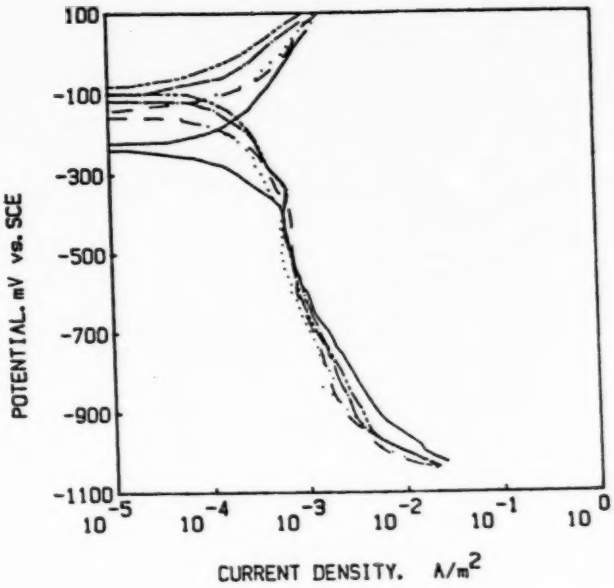


Fig. 4 Repeated polarization curves for one sample from Set B. the age of the sample at the beginning of each test was: curve 1——— 12 weeks; curve 2..... 15 weeks; curve 3 – – – – – – 22 weeks; curve 4 —·—·—·— 33 weeks; curve 5 ———·——— 35 weeks.

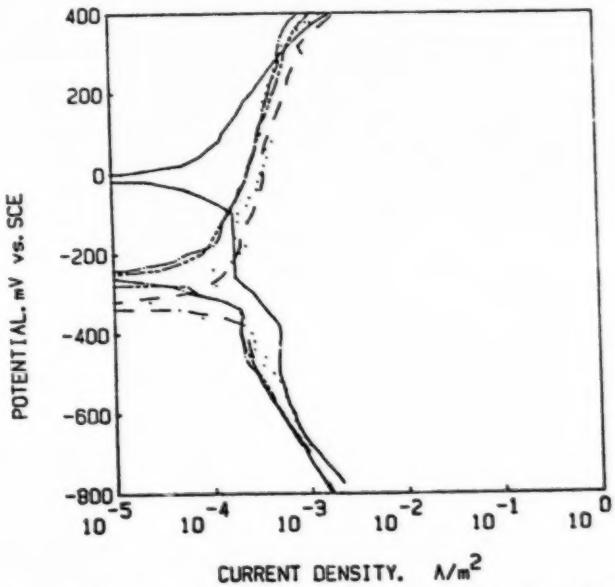


Fig. 5. Repeated polarization curves for one sample from Set C: the age of the sample at the beginning of each test was: curve 1——— 12 weeks; curve 2..... 15 weeks; curve 3 – – – – – – 22 weeks; curve 4 —·—·—·—·— 33 weeks; curve 5 ———·—·—·— 35 weeks.

As for the curves in Fig. 2, the E_{corr} values showed considerable scatter whereas the current values were quite reproducible.

It should be noted here, however, that none of these samples was actively corroding and the effects of large degrees of polarization may be greater for heavily corroding samples.

For field measurements, the time required to obtain the curves is the major disadvantage. Firstly, it severely limits the number of measurements that can be made and secondly it gives rise to problems of stability in the measurements. The polarization curves that have been obtained from steel in concrete in the laboratory [3-7] have been for samples immersed in water or other aqueous solutions. Under those circumstances, there is no problem with changing humidity or temperature during the measurements. For structures which are not immersed, on the other hand, the wetting of the surface necessary to obtain good electrical contact with the reference electrode and counter electrode can lead to changes in the humidity during the measurements. During experiments in the laboratory on samples in the atmosphere, it was found necessary to rewet the contacts periodically and this gave rise to a sharp increase in corrosion current and, consequently, peaks in the curves.

TAFEL LINE EXTRAPOLATION

In this method, described for steel in concrete by Hakkarainen and Ruohomäki[10] a small part of the polarization curve is determined experimentally and the data is then extrapolated theoretically to the Tafel regions using a computer program "Betacrunch"[11]. The program gives values of anodic and cathodic Tafel slopes and the corrosion current, as illustrated in Fig. 6.

Unfortunately, the values obtained were very sensitive to the number of data points used in the calculation. However, it is this author's opinion that a major contributing factor is that no compensation was made for ohmic drop across the concrete and this would result in the higher observed values of both Tafel slopes and corrosion currents with increasing levels of polarization, ie. increasing numbers of data points. It would be very useful to repeat the experiment using IR compensation.

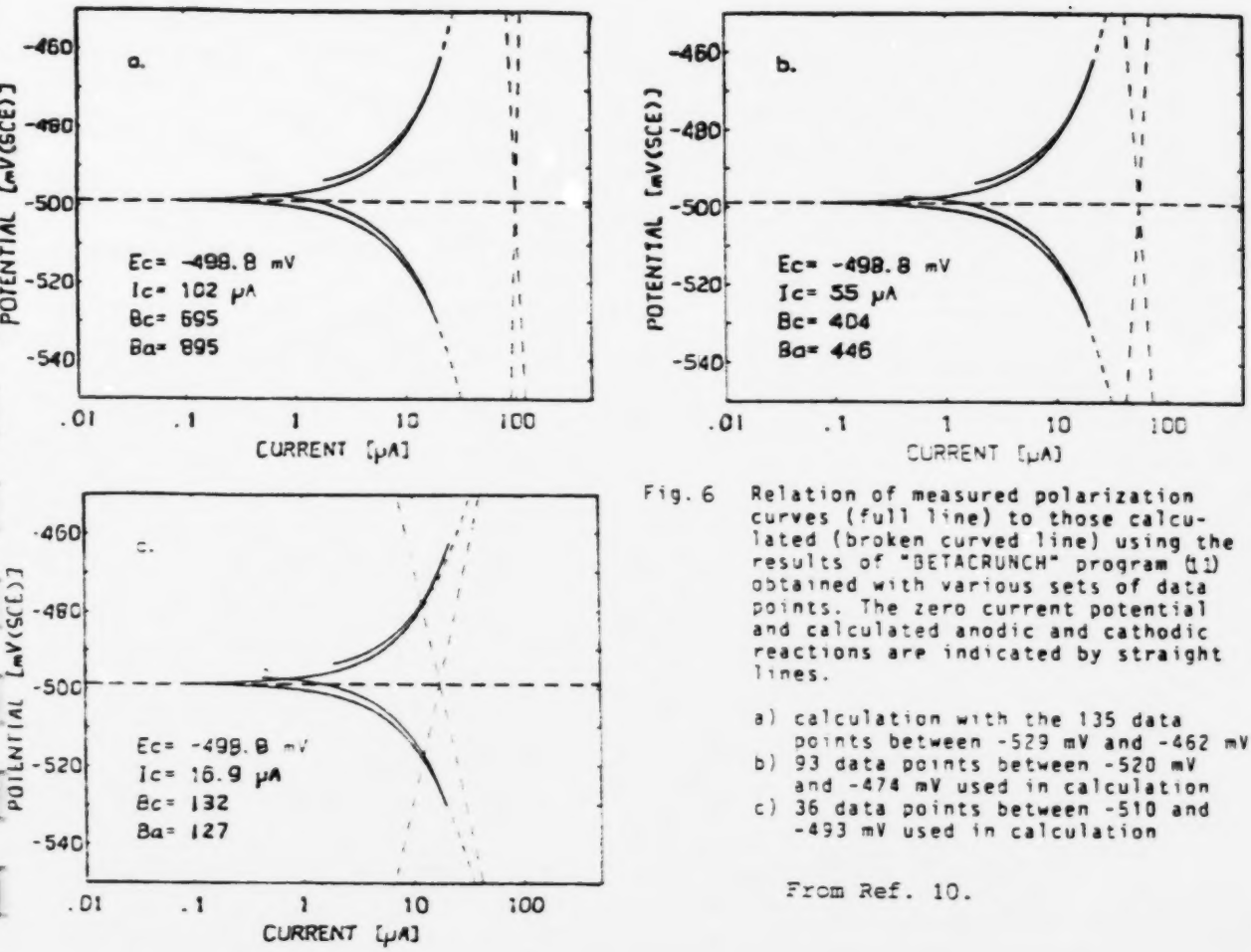


Fig. 6 Relation of measured polarization curves (full line) to those calculated (broken curved line) using the results of "BETACRUNCH" program (11) obtained with various sets of data points. The zero current potential and calculated anodic and cathodic reactions are indicated by straight lines.

a) calculation with the 135 data points between -529 mV and -462 mV
b) 93 data points between -520 mV and -474 mV used in calculation
c) 36 data points between -510 and -493 mV used in calculation

From Ref. 10.

POLARIZATION RESISTANCE MEASUREMENTS

In this technique,[12-14], the applied polarization is normally only 10 or 20 mV and, in this region, the relationship between potential and current is linear. The slope of the plot of potential vs. current is known as the polarization resistance, R_p, and is related to the corrosion current by:

$$i_{corr} = B/R_p$$

where B is a function of the Tafel slopes:

$$B = \beta_a \beta_c / 2.303(\beta_a + \beta_c)$$

Andrade and co-workers, [15-18], have made a large number of measurements using this method and made convincing correlations with gravimetric measurements on the same samples.

The exact method of obtaining polarization resistance values can vary considerably as is obvious from the descriptions given in Section III below. One of the more important variables is the sweep rate or step rate at which the potential or current is applied. If this rate is too high the structure does not have time to react adequately whereas if it is too low, it is possible that some changes may occur at the steel interface. In order to determine the minimum time required for "steady state" to be reached, my colleagues Jozsef Berecz and Erling Nielsen have calculated the response of the circuit given in Fig. 7a to an applied square wave potential, Fig. 7b. The part of the circuit enclosed by the dashed line represents the steel in concrete in which R_e represents the electrolyte (concrete) resistance, C_{dl} the capacitance of the electrochemical double layer at the steel/concrete interface and R_t the charge transfer resistance, which is equivalent to the polarization resistance, R_p. The calculations are given in the appendix and result in a current variation with time as shown in Fig.6c where the steady state is reached after approx. 100 ms.

Gonzalez et al.[19] have made similar calculations also assuming the steel-concrete system to be represented by the equivalent circuit shown within the dashed lines of Fig. 7a. They have shown that the time constant, τ_E, for potential controlled measurements is given by:

$$\tau_E = CR_e$$

whereas, for current control, the time constant, τ_i is given by:

$$\tau_i = CR_p$$

The authors argue that in the majority of real corroding systems $R_p >> R_e$ and, therefore, steady state is reached considerably faster in potential controlled measurements than in current controlled measurements. Even for potential controlled measurements, the time required for "steady state" conditions is the order of several tens of seconds. Moreover, it is clear that the higher the value of R_p the slower should be the sweep rate. At very slow sweep rates, the slope of E/i curve is equal to R_e+R_p but the value of R_p can be readily calculated if R_e is known or if $R_p >> R_e$.

Advantages of the polarization resistance technique

The major advantages of the technique are that it is rapid, simple, quantitative and the equipment costs are relatively low. Moreover, it does not require a detailed knowledge of the equivalent circuit or

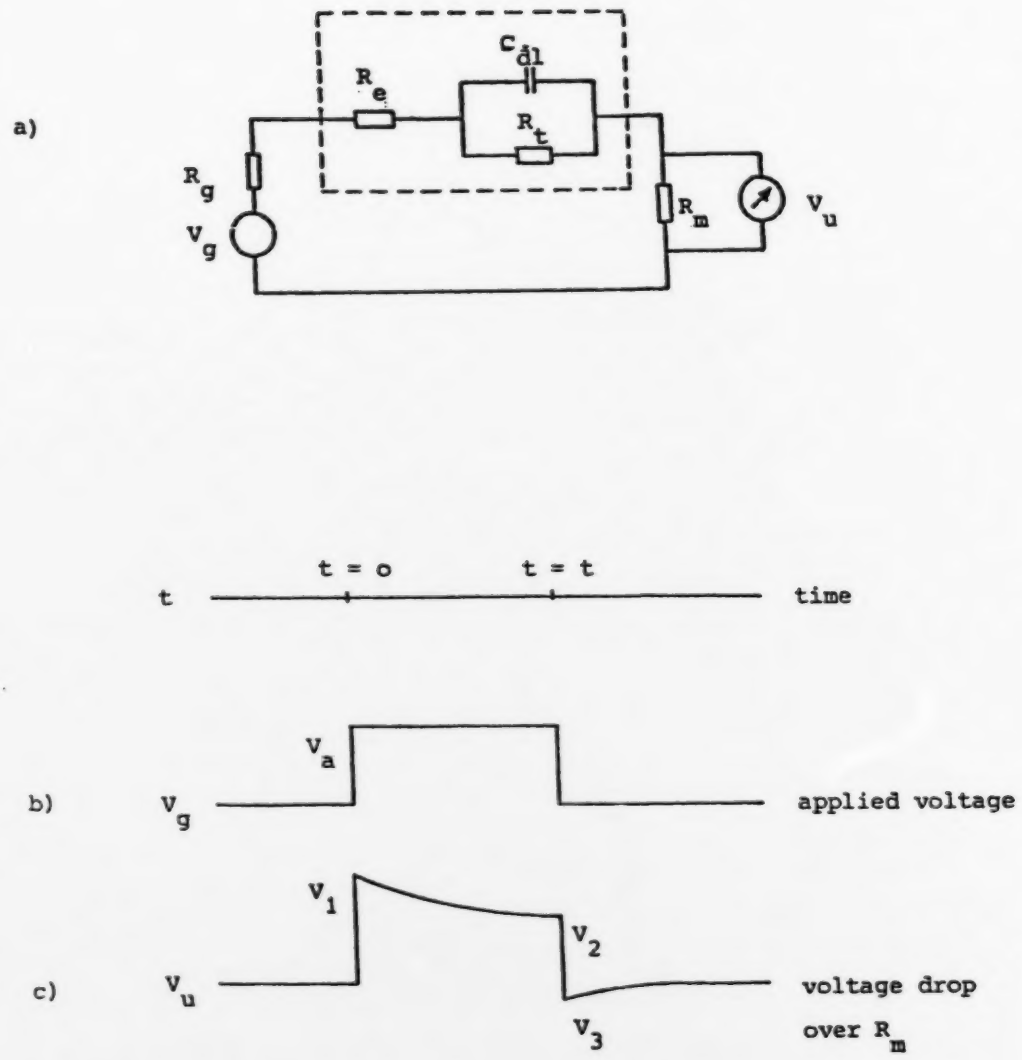


Fig. 7. (a) schematic circuit for polarization resistance measurement; that part of the circuit enclosed by a dashed line represents the steel in concrete; (b) the variation with time of the applied potential pulse and (c) the resulting current.

other factors for its interpretation. Each measurement can be made within a few minutes and a quantitative value of the corrosion rate can be simply calculated.

The time required for measurement has already been discussed and, especially for potential controlled systems, it is significantly faster than all of the other techniques.

From equipment, measurement and interpretation viewpoints, it is a simple method. Suitable equipment is readily available at reasonable cost and the method does not suffer from many of the disadvantages named above for polarization curve determination.

Until this year, all measurements at the Danish Corrosion Centre have been made on samples held under water. Therefore, a limited series of experiments have been performed on chloride-containing mortar samples in the laboratory atmosphere after exposure to different relative humidities. The aim was to confirm Andrade's opinion that such measurements are, indeed, easy and reliable and that the wet contact between the external electrode(s) and the mortar does not significantly change the sample's humidity during the course of the measurement. A damp sponge was used for this contact and proved to be perfectly adequate for the length of time required for the test. In these tests, the potential was changed in steps of 1mV/15s from $E_{corr} \rightarrow E_{corr}+10$ mV $\rightarrow E_{corr}-10$mV $\rightarrow E_{corr}$ and a typical curve of the data is shown in Fig.8. The effect of scan rate has also been investigated but did not have a significant effect on the results within the range of scan rates tested.

While the method is easy and reproducible and gave no problems with regard to holding the humidity constant for the length of the test, it was obvious from the results that IR compensation is necessary for tests carried out in the atmosphere. IR compensation is not available on the custom-made equipment at the Danish Corrosion Centre because it has not been considered warranted before in view of the values of resistance and current involved in submerged samples. However, the resistance of samples tested in the atmosphere is several orders of magnitude higher than it is for water saturated samples and it is clear that some form of IR compensation must be incorporated in the equipment for measurements on non-submerged samples.

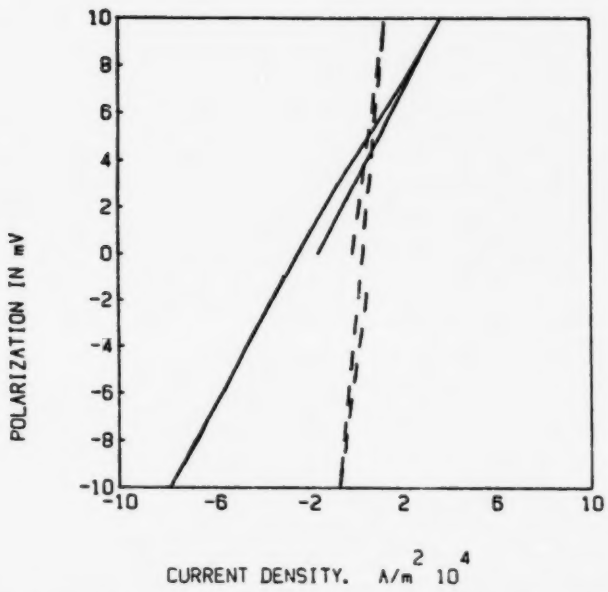


Fig. 8. Potentiostatic polarization resistance scan of two samples, one corroding at a rate of 3.10^{-3} A/m^2 (———) and the other at a rate of 5.10^{-4} A/m^2 (-----)

Disadvantages of the polarization resistance technique

The limitations of the technique in general have been discussed by many authors [19-22] and have been excellently enumerated by Gonzalez et al.[19] as:

1) the Tafel slopes are unknown or vary with time;
2) lack of linearity of the polarization curve in the vicinity of the corrosion potential;
3) the medium has a very high resistivity due to the electrolyte itself or the corrosion product layers;
4) the corrosion potential varies during the measurement;
5) there is pitting or localised corrosion;
6) the corrosion reaction is controlled by diffusion or the metal is passivated;
7) the equilibrium potentials of anodic or cathodic half cell reactions are very close to the corrosion potential;
8) the system being polarized requires a given time to reach steady state;
9) perturbations in the working electrode-electrolyte interface during measurement.

All of these limitations can apply to the steel-concrete system! However, in the author's opinion, one cannot expect to be able to determine corrosion rates of steel in concrete, in the laboratory or in practice, more exactly than within an order of magnitude and, with that proviso, the above limitations can either be overcome or their effects are not sufficiently large to cause large errors in the measurement of R_p.

A.C. IMPEDANCE MEASUREMENTS

In sequential A.C. impedance measurements, a sine wave of fixed amplitude, usually of the order of 10 mV, is applied to the embedded steel at decreasing frequencies, typically from 100 kHz to 1 mHz and both the phase shift and modulus of impedance of the steel are monitored as a function of frequency. A review of the technique and its application to steel in concrete are given in Refs. 23 and 24, resp.

Alternatively, one can apply a potential pulse of random frequency and fixed amplitude. Both the applied and responsive spectra are then analysed by fast Fourier transform (FFT), as described in Ref. 25. Its advantage is that it is faster than the sequential method but the available frequency range on commercial equipment is smaller.

For both methods, the response is interpreted in terms of an equivalent circuit composed of resistors and capacitors such as that shown in Fig. 9a. The complex plane response of this circuit is given in Fig.9b and is known as a "Nyquist plot". Unfortunately, the case of steel in concrete is not so simple because the system has a very high resistance, frequently has a passive film and corrosion is often controlled by diffusion. The alternative analogue circuits shown in Fig. 9 have, therefore, been proposed for steel in concrete.

Advantages of A.C. impedance measurements

Its greatest advantage is that information concerning diffusion rates, the existence of passive films, etc. can be obtained by this method. It is, therefore, an excellent research tool for investigating the mechanisms of corrosion and the effect of different concrete and steel parameters on the mechanism and rate of corrosion. A second advantage is that, like polarization resistance measurements, only a small potential is applied to the steel. In this case it is also an alternating pulse and it is unlikely that it will have any significant effect on the local environment at the steel surface.

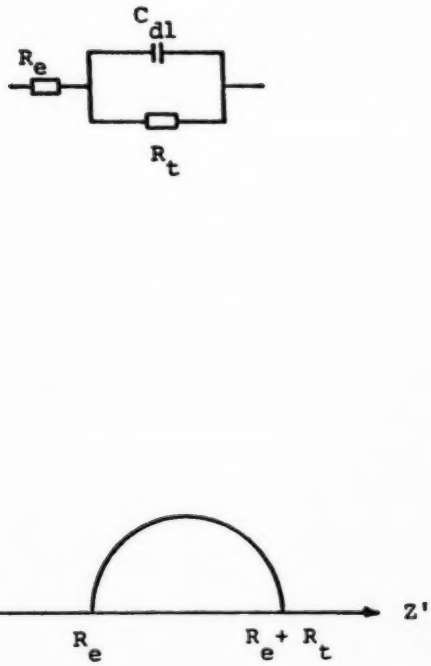


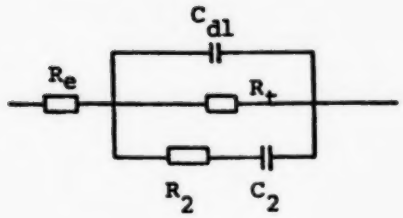
Fig. 9. (a) equivalent circuit for corrosion of steel in concrete and (b) the complex plane response of this theoretical circuit, commonly known as a "Nyquist plot".

Disadvantages of A.C. impedance measurements

Firstly, the system's equivalent circuit should be known and, as indicated above, there is no general agreement on the most appropriate circuit for steel in concrete. Moreover, it is possible that a single equivalent circuit is not adequate to describe all concrete structures and that the characteristics of the particular structure must be known before the most appropriate equivalent circuit can be chosen. For monitoring of structures, this is simply not practical.

Secondly, the corrosion rates of steel in concrete are normally so slow that even in actively corroding systems, the semicircle on the Nyquist plot is not complete within the available frequencies and extrapolation is necessary in order to obtain a value of the corrosion rate [29]. In systems controlled by diffusion or with passive films or corrosion products, quantitative corrosion rates cannot be obtained.

a)



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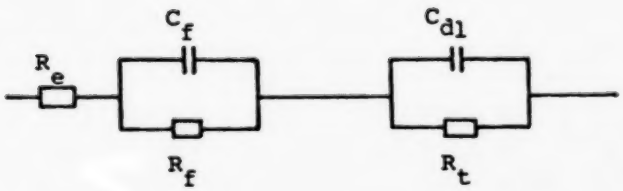
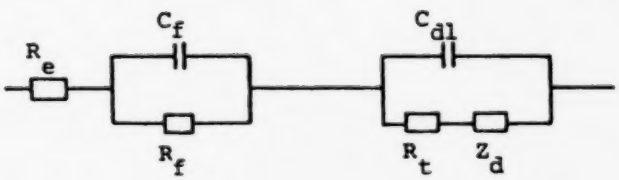


c)



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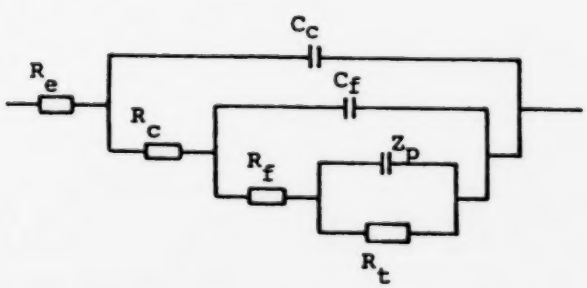

Fig. 10. Alternative equivalent circuits for corrosion of steel in concrete. R_e, R_t and C_{dl} are as in Fig. 7. R_f and C_f represent film controlled processes, R_c and C_c represent the effect of corrosion products or cement structure such as layers of Portlandite at the steel/cement interface. (a) from Ref.27; (b) from Ref. 26; (c) from Ref. 24; (d) from Ref. 28.

Thirdly, the measurements take a long time to complete which means that very few measurements can be made in a given time. In addition, the corrosion potential can shift during measurement and the difficulties described above for polarization curve measurements, in keeping a good contact between the external electrodes and the concrete without changing the humidity of the concrete, would also apply to A.C. impedance measurements.

A fourth disadvantage is that the equipment costs are significantly higher that those necessary for other techniques and the currently available models are not well suited to field work.

CURRENT TRANSIENTS

This new method, under development by Andrade and her co-workers, can be described as a compromise between polarization resistance measurements and A.C. impedance measurements. As described by Andrade et al. in Ref. 27, a 10 mV square wave pulse of, eg., 30 s duration is applied to the embedded steel and the current response is monitored using an oscilloscope. The time constants for the decay of the current are determined and, using an equivalent circuit for the system, in this case, that given in Fig.10a, quantitative values of corrosion rate together with information concerning passive films and diffusion rates, etc. can be obtained. As the method has not yet been fully evaluated, I cannot comment on it further.

ELECTROCHEMICAL NOISE MEASUREMENTS

The fluctuations in electrochemical potential which naturally occur between two embedded electrodes or between an embedded electrode and an external reference elctrode can be related to the electrochemical activity at the surface of the electrode(s). Dawson et al. [30] have applied such potential "noise" monitoring to steel in concrete. The noise is monitored over a period of time (typically 15 min. - 2 hrs.) and the spectrum analysed by either fast Fourier transform (FFT) or by the maximum entropy method (MEM). Typical results, taken from Ref. 30, are shown in Fig.11 for non-corroding steel in concrete and in Fig. 12 for steel in conrete contaminated by chloride. It is reported that the standard deviation of the noise signal is proportional to the corrosion rate.

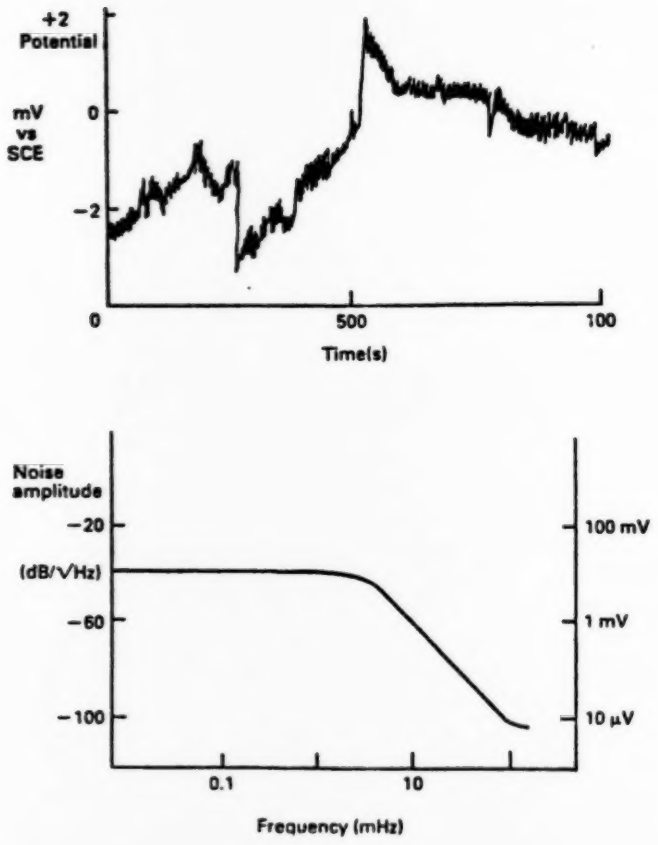

Fig. 11 Electrochemical Noise measurements for steel in uncontaminated concrete; (a) potential/time record and (b) noise spectrum (from Ref.30).

In addition, Paul Langford at UMIST has begun to investigate current noise measurements in which he monitors the variations in current flowing between the embedded steel and an external Pt electrode. Since there is a small shift in the potential of the steel when it is connected to the Pt electrode, the ratio of potential shift to current can be used as the polarization resistance. The method is currently under evaluation and its reliability cannot yet be confirmed.

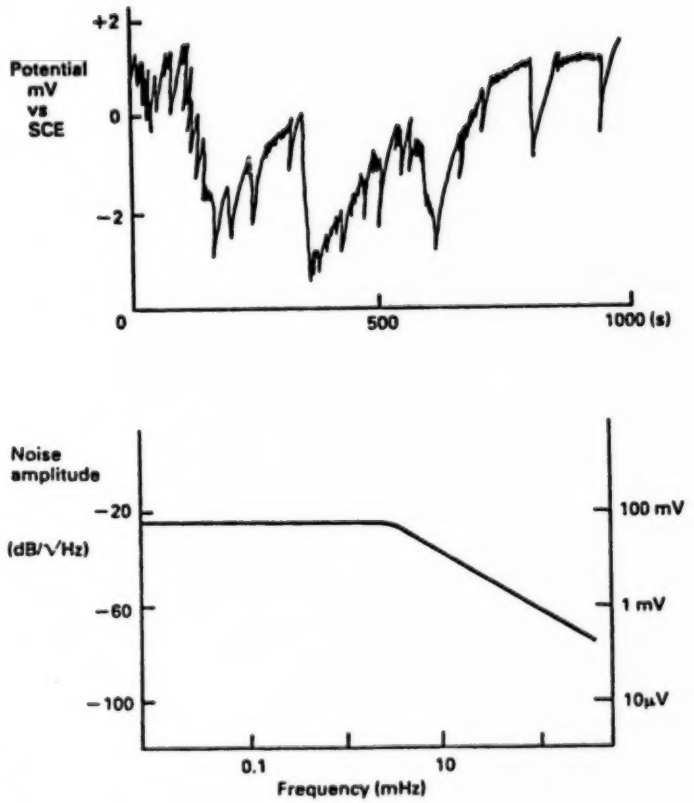

Fig. 12. Electrochemical noise measurements for steel in chloride contaminated concrete; (a) potential/time record and (b) noise spectrum (from Ref. 30).

Advantages of the electrochemical noise technique

The major advantage of the technique is that no potential or current is applied to the steel and, therefore, the technique does not change the system in any way.

Disadvantages of the electrochemical noise technique

Quantitative results cannot be obtained by the technique. It also has the same disadvantage as the A.C. impedance and polarization curve techniques in that it takes a long time to obtain the measurements.

III. SUMMARY OF VISITS

1. QUEEN'S UNIVERSITY, KINGSTON, ONTARIO, CANADA

Personnel: Dr. Brian Hope, Civil Engineering
Dr. John Page, Electrochemistry
Dr. John Poland, Analytical Chemistry
Dr. Michael Bell, Physics

Techniques used:

1) Linear Polarization:

Linear polarization tests were made by applying a single 4 mV square pulse of 1 ms duration to the embedded steel and monitoring the current response on an oscilloscope and taking the ratio of applied potential, E, to current, i, as the polarization resistance, R_p. Occasionally, a second pulse of 8 mV amplitude was applied to check the linearity of the E/i relationship. The corrosion current, i_{corr}, was calculated assuming β_a and β_c to each be 100 mV/decade.

2) A.C. Impedance:

A Solartron Transfer Function Analyser (TFA) was used to apply a cyclic 10 mV pulse to the embedded steel at sequential frequencies and the response was analysed in terms of the analogue circuit given in Fig. 10c.

Materials tested

No field measurements have been made. Laboratory tests[31] were made on 64 x 300 x 400 mm^3 slabs containing three electrodes, two of which were used as working electrodes, the third as a counter electrode. An external $Cu/CuSO_4$ reference electrode was connected to the concrete via a wet sponge.

Conclusions:

The linear polarization technique used was not considered to be satisfactory because it could not differentiate between corroding and non-corroding samples. This is almost certainly due to the pulse duration being too short. As discussed above, at least several seconds are required for the system to react.

The a.c. impedance method was considered to be a useful tool to differentiate corroding from non-corroding steel but could not readily give a quantitative value of the corrosion rate. Interpretation of the typical data for steel in concrete shown schematically in Fig.13 was that a line with a slope >45° indicates that the system is dominated by a high passive film resistance and cannot, therefore, be corroding, whereas a slope <45° indicates the system to be under diffusion control and to be actively corroding.

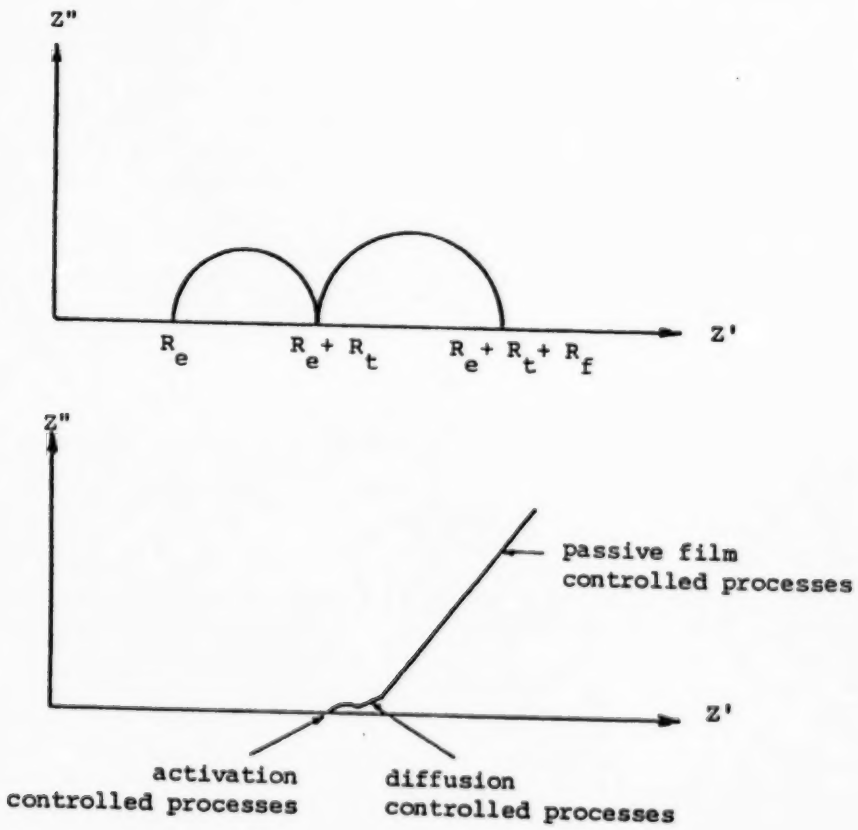

Fig. 13 Schematic diagram of (a) theoretical and (b) experimental Nyquist plots for steel in concrete according to the equivalent circuit shown in Fig. 10b (Ref. 26).

2. THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D.C., USA.

Personnel: Dr. Edward Escalante
Dr. Y. Paul Virmani (U.S. Federal Highway Administration)
Dr. Neville Pugh

Techniques used:

1) Linear Polarization

Linear polarization tests were made galvanostatically by applying a periodic current pulse of 3.0s on and 0.3 s off and monitoring the corresponding potential with either a digital oscilloscope (Nicolet 3091) or a datalogger (HP3421A). The reason for this on/off ratio is that it is hoped that the steel will be cheated into thinking that it is receiving continuous current. As discussed in Section II, this is probably not the case, 300 ms being of the the order of the time required to achieve steady state[28] and, therefore, too long for this purpose.

The potential is measured at the "instant current off" point indicated in Fig. 14 in order to overcome the ohmic drop across the concrete and the amplitude of the current pulse is slowly increased until the measured potential is a steady 10 mV. The current is then controlled to maintain this voltage for three minutes. The current initially relaxes and after it reaches a more or less steady state, the ratio between the potential, E, at the instant current off, and the steady state current is taken as the polarization resistance. The corrosion current is then calculated assuming anodic and cathodic Tafel slopes of 100 mV/decade. One complete measurement can take up to half an hour. This work is reported in Ref. 30.

2) A.C. Impedance

Some tests were made using sequential a.c. measurements similar to those made at Queen's University but at the time of my visit, the data had not been analysed.

Materials tested:

The computer controlled system has been used to monitor the corrosion of 10 single electrode mortar samples immersed in $Ca(OH)_2$ solution over a few months and reasonable qualitative agreement has been

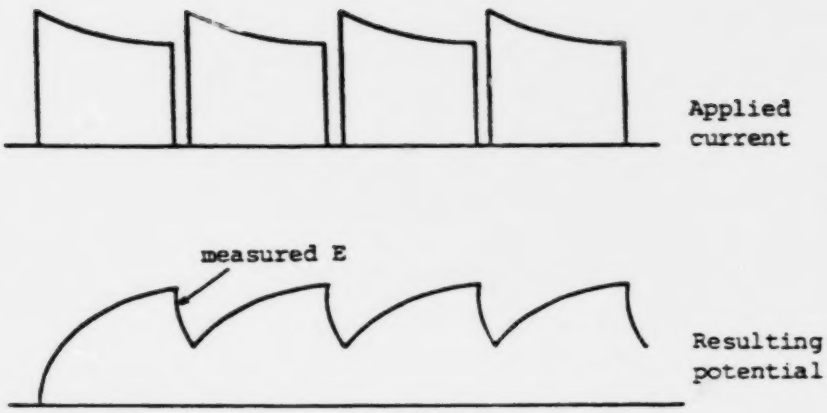

Fig. 14. Schematic diagram of applied current pulse and resulting polarization used for polarization resistance measurements at NBS.

obtained between the measurements and the visual evaluation of the degree of rusting of the electrodes.

Manual measurements had been made on two bridge decks but I have not seen reports of the measurements and heard only that they were considered satisfactory. At the time of my visit, it was planned to make computer controlled measurements of bridge decks over a period of several months. The counter electrode to be used in field measurements was a 10 cm square steel block with a central hole to support the $Cu/Cu/SO_4$ reference electrode. Contact to the concrete was via a wet sponge.

I have since had a report by telephone of the measurements made in the Autumn of 1985. Three bridges were monitored and several practical problems were encountered before the measuring system could be made to function satisfactorily. These included: (1) discontinuities in the cabling which was rectified by having the computer check the continuity immediately prior to each measurement; (2) noise in the a.c. line to the oscilloscope which was overcome by using a battery driven model; (3) burning out of part of the equipment by incorrect wiring and (4) severe flooding!

I name these because what are simple problems to overcome in the laboratory are major obstacles in the field.

After these problems were overcome measurements were obtained which gave apparently satisfactory results. No confirmation of this is available, however, because the reinforcement has not been examined. Nevertheless, the results are considered to be sufficiently satisfactory to warrant continuation of the program. Thus, five bridges in Pennsylvania will be repeatedly monitored during the Summer of 1986, and, when the measurements are completed, cores will be taken to establish the validity of the results.

Conclusions

The linear polarization method was considered preferable to a.c. impedance on the basis of instrument cost, the time required to perform the experiments and the ease of interpreting the results.

3. UNIVERSITY OF MANCHESTER INSTITUTE OF SCIENCE AND TECHNOLOGY, MANCHESTER, ENGLAND.

Personnel Dr. Gareth John, CAPSIS
Dr. John Dawson
Dr. Paul Langford

Techniques used:

1) Polarization Resistance

Paul Langford has made polarization resistance measurements as part of his thesis work, sweeping the voltage dynamically at 5 mV/min, from the corrosion potential to +20 mV and reversing the sweep to-20mV.

2) A.C. Impedance

UMIST have been the pioneers in the use of a.c. impedance for investigation of corrosion of steel in concrete in the laboratory and have interpretated the data in terms of the equivalent circuit given in Fig.10b. However, they have not yet used the method for field measurements.

3) Electrochemical Noise

Electrochemical noise measurements are normally made by monitoring the potential fluctuations between either two embedded electrodes or bet-

ween one embedded electrode and an external saturated calomel electrode. As mentioned above, however, Paul Langford has also attempted current noise measurements.

Materials tested

A large number of laboratory samples with single or double embedded electrodes has been tested over the last few years but the only practical construction to be monitored was a retaining wall which was surveyed by both electrochemical noise and by potential mapping.

An important new innovation, first suggested by Escalante[33] and put into practice by Langford is the guard ring counter electrode. A second counter electrode, controlled by a separate potentiostat, surrounds the primary counter electrode and, thereby, limits the area of reinforcement contributing to the measured current. This has been used by Langford in both conventional polarization resistance testing and in current noise measurements and is claimed to improve the reproducibility of the results.

Conclusions

The potential noise measurements are claimed to be able to distinguish between passive and active regions of the reinforcement and between pitting and general corrosion, but do not give quantitative corrosion rates. A.C. impedance, on the other hand, is considered to give quantitative data if the steel is actively corroding but not if it is passive.

4. UNIVERSITY OF ASTON, BIRMINGHAM, ENGLAND

Personnel: Dr. Christopher L. Page

Techniques used:

1) Linear Polarization:

Two methods of obtaining polarization resistance data are used. The first is a potentiodynamically controlled sweep from E_{corr} → -20 mV → +20 mV at 10 mV/min. The slope of the E vs. i curve is used as the polarization resistance. The second is an automatic system, an AMEL Model 551 potentiostat with a feedback IR compensation system, which one turns on, sets to +10 mV, waits 30 s and reads the value of current. R_p is taken as the ratio of E/i.

2) A.C. Impedance

A Hewlett Packard Spectrum Analyser, is used for the FFT method as described in Section II.

3) Electrochemical Noise

The standard deviation of the potential fluctuations between two embedded electrodes is being determined and compared with linear polarization measurements on the same samples in order to ascertain whether the "noise" can be used as a measure of corrosion rate.

Materials used

A large number of mortar and concrete samples with one or more embedded electrodes has been investigated. The primary aim of Page's research has been to investigate the mechanisms of reinforcement corrosion and the influence of concrete parameters, rather than measuring techniques. No field measurements have been made by this group.

Conclusions

For quantitative measurements of corrosion rates, Page considers linear polarization measurements to be the only currently available method. Polarization curve measurements and A.C. impedance take too long and could, therefore, change the environment at the steel/concrete interface. Moreover, for quantitative A.C. measurements, extremely low frequencies are necessary. For research investigation of eg. passive films, the method was considered to be a very good tool. The electrochemical noise measurements were more promising than expected but they too were not appropriate for quantitative rates of corrosion.

On the basis of commercial experience with potential mapping, Page is very sceptical about the use of corrosion rate measurements in the field before considerably more research has been made in the laboratory on large structures by qualified personnel. He also expressed the opinion that, because any corrosion system is dominated by the behaviour of the smaller of the two half cells, the behaviour of the small, external counter electrode would dominate the measurements on practical reinforcing systems.

5. INSTITUTO EDUARDO TORROJA DE LA CONSTRUCCIÓN Y DEL CEMENTO, CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS, MADRID, SPAIN

Personnel: Carmen Andrade

Techniques used:

1) Polarization Resistance:

I believe that Andrade and her co-workers were the first to apply polarization resistance measurements to the determination of reinforcement corrosion rates and they have been making such measurements for the last 13 years. As mentioned in Section II, considerable effort has been expended on evaluating the technique, its accuracy, reproducibility, advantages and limitations[11-17]. The polarization results show very good agreement with gravimetric measurements and have allowed realistic Tafel constant values to be determined[15,17]. The two variations of the techniqes used are the same as those used by Page et al.

2) A.C. Impedance:

Both the sequential and simultaneous techniques described above, using a Solatron Transfer Function Analyser and a Hewlett Packard Spectrum Analyser, respectively, have been used. A comparative discussion of A.C. impedance and polarization resistance measurements is given in Refs. 29 and 34.

3) Current Transients:

This new technique, under development by Andrade, appears to be a practical compromise between polarization resistance measurements and A.C. impedance measurements. It is described in Section II.

Materials tested:

The majority of samples tested have been small mortar prisms with two steel "working" electrodes and one graphite "counter" electrode centrally placed between the two steel rods. However, progressively larger samples are being tested with a view to determine the practicality of using corrosion rate measurements in the field. The largest samples tested to date are two approx. 2 x 2 m^2 "walls" with embedded reinforcement mats.

Conclusions:

Andrade preferred polarization resistance measurements or, possibly, current transient measurements, to A.C. impedance primarily because of the time necessary to complete the test. Similarly, potential-controlled- rather than current-controlled-polarization resistance measurements are preferred for the same reasons. Considerable concern was expressed about measurements which take longer than a few minutes affecting the environment adjacent to the steel even with a polarization of only 10 mV.

Andrade was emphatic that some form of IR compensation was essential and preferred the "instant current off" method to a feedback system. It should be noted, however, that the major problem in Spain is carbonated concrete which is not water saturated. Under those circumstances, both the current and the resistance are high and the IR drop is significant.

A second point on which she was emphatic was the use of a small counter electrode to localise the measurements in a large structure.

Her opinions concerning corrosion rate measurements on real structures were similar to those expressed by Page, that more laboratory research is necessary before the measurements can be relied upon, but agreed that now was the time to begin to evaluate practical measurements.

IV. CONCLUSIONS AND RECOMMENDATIONS

Field Measurements

It is clear from the above that the only currently available method of measuring corrosion rates of steel in concrete suitable for practical (field) measurements is the polarization resistance technique. The advantages of this technique for this purpose are overwhelming and include:

- -rapidity of measurement;
- -relatively simple and inexpensive equipment required;
- -quantitative data can be readily obtained

For field measurements, as simple a system as possible should be used. From my own experience, I would strongly recommend commercially avail-

able equipment rather than custom made systems for the following reasons: (i) commercial equipment has been tried and proven by a large number of users and the teething troubles have been overcome or it would not still be on the market; (ii) the instruments are covered by a guarantee and professional service is available if needed; (iii) (iii) identical back-up systems can readily be obtained and (iv) it is accompanied by an instruction manual!

For the reasons excellently put forward by Gonzalez et al., potential control rather than current control is to be recommended and fairly rapid sweep rates, eg. 10 mV/min, can be used. A triangular sweep from = 0 → +10 → -10 → 0 would thus take 4 mins. to complete. Including placement of the electrodes and a waiting period of 5 mins. to allow stabilization of the system before measurement, each data point could be obtained within 10 - 15 mins. enabling one to obtain approx. 50 data points per day.

The measuring system should include a commercial potentiostat which must be battery operated to avoid noise problems associated with line power supply and allow measurements in areas where access to the line power supply is not available. The potentiostat should have automatic IR compensation, preferably by the current interrupt method, and facilities for determining circuit resistance. It must also have computer control possibilities: it is not practical to make and record all the settings and to read the data off an oscilloscope and record it by hand in a notebook under field conditions! Pre-programming the system in the laboratory to allow for automatic measurement with the minimum of operator interaction is an advantage and automatic storage of the data is essential.

The automatic Waverley potentiostat is no longer available but the Princeton Applied Research unit or the Solartron Electrochemical Interface unit are possible candidates. A system consisting of such a potentiostat coupled to a portable computer, such as the Hewlett Packard 85 would cost of the order of Can.$ 20,000-25,000. The same system could be used to make complete polarization curve measurements.

For the counter electrode, a steel block with a central hole to support the reference electrode, such as that used by Escalante, is to be recommended. Moreover, the use of a guard ring appears to be an

excellent and simple solution to the problem of defining the area of reinforcement contributing to the measurements and should be investigated further.

Laboratory Measurements

For laboratory measurements of the effect of cement composition, additives, etc. on the behaviour of steel in concrete and, for example their effect on the chloride pitting potential, the use of polarization curves is to be recommended. For automated measurements, the instrument costs would be the same as for polarization resistance measurements, ie. of the order of Can.$20,000 - 25,000. For parallel measurements on a large number of similar samles, a data logger is needed in addition to the potentiostat and computer and this would cost an additional Can.$6,000 - 10,000, depending on the number of channels required.

In order to improve our understanding of the mechanisms of corrosion and the role of interface films, diffusion, etc. A.C. impedance or current transient measurements are to be preferred. For impedance measurements, the instrument costs would be of the order of Can.$35,000 - 45,000 depending on whether or not computer control was required.

It should be noted that the instrument costs given are only rough estimates because monetry exchange rates vary and import and freight charges are dependent on the origin of the instrument. The prices quoted are those obtained by the author in Denmark and are converted to Canadian dollars at the current rate of exchange.

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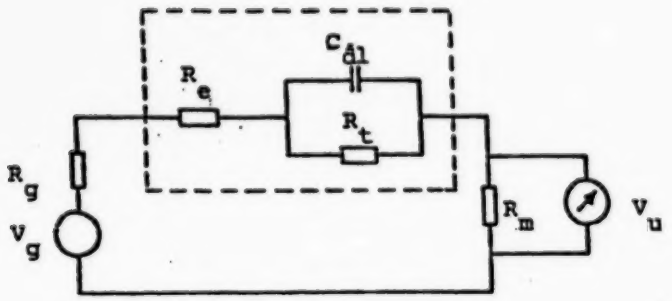
V. APPENDIX

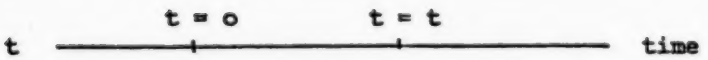
Calculation of the time required for steel to respond to an applied potential.

Erling Nielsen, the Danish Welding Institute
and
Jozsef Berecz, The Danish Corrosion Centre

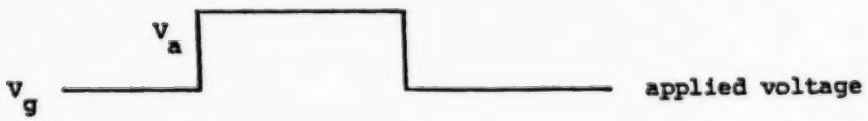
The following calculations are based on the measuring circuit given below.

a)

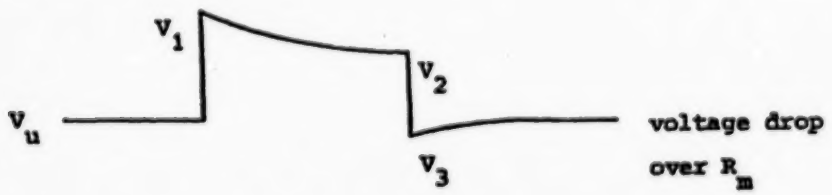




b)



c)



$$R_{eff} = R_t(R_e + R_m + R_g)/(R_t + R_e + R_m + R_g)$$

$$= C_{dl} \cdot R_{eff}$$

$$V_1 = V_s \cdot R_m/(R_e + R_m + R_g)$$

$$V_2 = \frac{V_a \cdot R_m}{R_e+R_t+R_m+R_g} + \left(\frac{V_s \cdot R_m}{R_e+R_m+R_g} - \frac{V_s \cdot R_m}{R_t+R_e+R_m+R_g} \right) \cdot e^{-t/C_{dl}R_{eff}}$$

$$V_3 = V_2 - V_1$$

The potential over the measuring resistance, V_u is given by:

$$V_u = \begin{cases} t<0 & 0 \\ 0<t<t_1 & V_s \cdot R_m \left[\frac{1}{R_x} + \left(\frac{1}{R_x - R_t} - \frac{1}{R_x} \right) e^{-t/C_{dl}R_{eff}} \right] \\ t_1<t & V_3 \cdot e^{-t/C_{dl}R_{eff}} \end{cases}$$

where $R_x = R_e+R_t+R_m+R_g$

Assuming $R_e = 100\,\Omega$, $R_m = 100\,\Omega$, $R_t = 10{,}000\,\Omega$, $C_{dl} = 10^{-5}$ F and $V_a = 10$ mV, the following variation of V_u with time is obtained: